

## TITLE OF THE INVENTION

### METHOD OF STORING MATERIAL INTO WHICH GAS SATURATES

## FIELD OF THE INVENTION

5           The present invention relates to a technique which performs injection foaming or extrusion foaming by allowing a foaming agent such as an inert gas to saturate into a polymer and a rubber material, thereby obtaining a foamed product having a foamed interior.

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## BACKGROUND OF THE INVENTION

          Foam foaming has a long history. For example, techniques of obtaining resin foamed products by injection foaming are disclosed in USP3268639 and  
15   USP3384691. In recent years, methods of foam foaming using chemical foaming agents or physical foaming agents are described in textbooks of synthetic resin foaming.

          Lately, a method of foaming a very small foam  
20   called a microcell is found in Massachusetts Institute of Technology, U.S.A. This method and an apparatus for the method are disclosed in USP4473665, USP5158986, USP5160674, USP5334356, USP5571848, and USP5866053. In the method and apparatus proposed in Massachusetts  
25   Institute of Technology, U.S.A., a supercritical inert gas is blown into a portion where a resin is melted in a plasticator of an injection foaming machine, and the

well-melted resin and the gas are mixed by a static mixer. It was reported that when the pressure and temperature were controlled, a large number of cells of 25  $\mu$ m or less were evenly dispersed in the foamed  
5 foamed product, and the foamed product had almost no strength deterioration since the cell size was small. The above references also describe a method by which a resin material is placed in a pressure vessel, a supercritical inert gas is allowed to saturate into the  
10 resin material, and the resin is foamed by abruptly reducing the pressure at a temperature near the melting temperature of the resin, and a method by which the resin is foamed by abruptly raising the temperature after the temperature and pressure are once lowered.

15 Japanese Patent Laid-Open Nos. 8-85128 and 8-85129 describe methods by which a pressure-resistant chamber is attached to a hopper of an injection foaming machine, and a gas is allowed to saturate into a molten resin or resin pellets at a high pressure, thereby  
20 foaming the resin.

That is, the conventional foam foaming is roughly classified into chemical foaming and physical foaming. The chemical foaming includes a master batch method in which a foaming agent which causes a chemical reaction  
25 by heat and a resin material are mixed in the form of pellets, and a method in which the foaming agent is kneaded in a resin material. The physical foaming

includes a method in which an inert gas is allowed to  
directly saturate into a molten resin from a  
plasticator of an injection foaming machine or extruder,  
and a batch method in which an inert gas is allowed to  
saturate into a previously foamed and shaped resin  
product at a high temperature and high pressure, and  
the resultant material is foamed in a pressure vessel  
by abruptly changing the temperature or pressure.

In the conventional chemical foaming, the master  
batch method by which a heat decomposable foaming  
material and a resin material are mixed immediately  
before foaming is often used. Unfortunately, this  
method has many problems such as harmfulness, foam  
corrosion, the worsening of the foaming environment,  
and the difficulty of handling. In contrast, the  
physical foaming is harmless and causes no foam  
corrosion, and nitrogen and carbon dioxide exist in  
natural air. Therefore, the physical foaming is  
regarded as superior to the chemical foaming. However,  
in the method of allowing an inert gas to saturate  
directly into a molten resin, the gas is directly blown  
into the molten resin material, so a portion of the  
molten resin in contact with the gas is rapidly cooled  
when the gas is blown. If the gas is continuously  
blown, a large portion of the molten resin is cooled.  
Consequently, the viscosity rises, and it takes a long  
time to restore the resin temperature and viscosity

suited to foaming.

Also, when a gas is heated to a temperature close to the melting temperature of a resin in advance, the volume of the gas increases with the temperature rise.

5 Therefore, if the gas is directly blown into the molten resin, the foaming magnification after the resin is charged into a foam significantly decreases because the internal pressure of the resin is low.

Furthermore, to compensate for this drawback, it  
10 is possible to raise the pressure together with the gas temperature, and blow the gas into the molten resin while the gas concentration is maintained. In this method, however, the gas pressure is very high, and the gas flows into the molten resin at the moment when the  
15 gas is blown into it. This makes it difficult to control the gas blowing amount, and increases variations in amount of the gas which saturates into the resin. Also, since the gas is abruptly blown into the molten resin, the molten resin forms two separated  
20 layers of the gas and resin near the blowing port. To evenly disperse the gas in the resin, therefore, it is necessary to mechanically repeat kneading by using a static mixer or the like, and encourage dissolution of the gas into the resin by raising the pressure of the  
25 resin-gas mixture itself. This complicates the apparatus, and variations in gas saturation amount in the material vary the dimensional accuracy of the

foamed product and deteriorate the product quality. In addition, the long cycle deteriorates the productivity.

The batch method using an inert gas eliminates both the drawbacks of the chemical foaming and the  
5 drawbacks of the physical foaming by which a gas is directly blown into a molten resin. However, since this batch method is an intermittent production method using batch processing, the productivity significantly worsens.

10 A method such as described in Japanese Patent Laid-Open No. 8-85128 in which a gas is allowed to saturate into a resin material by the batch method and then the material is continuously foamed by an  
15 injection foaming machine compensates for the above-mentioned drawbacks. However, the amount of gas which saturates into a solid resin material such as pellets changes in accordance with the gas pressure, temperature, and time. Accordingly, if the foaming  
20 cycle or gas saturation time changes even slightly, the amount of gas which saturates into a resin material changes. Since this changes the foamed state of the foamed product, the accuracy also changes.

#### SUMMARY OF THE INVENTION

25 The present invention, therefore, has been made in consideration of the above situation, and has as its object to obtain a high-accuracy foamed product with

high productivity.

To solve the above problems and achieve the object, according to a first aspect of the present invention, there is provided a method of storing a material into which a gas saturates, before the material is foamed in a metal foam, while maintaining a gas saturated state, wherein the material into which the gas saturates is stored at a predetermined ambient pressure and predetermined ambient temperature, thereby preventing escape of the gas from the material into which the gas saturates.

According to a second aspect of the present invention, there is provided a method of storing a material into which a gas saturates, wherein a gas is allowed to saturate into a resin material at a saturation pressure  $P$  (MPa) of 4 (MPa) or more and a temperature  $T$  ( $^{\circ}\text{C}$ ), and, letting  $m$  ( $-0.05 < m < 0.2$ ) be a coefficient determined by a material type and a gas saturation time, the material is stored in an ambient defined by a pressure  $p$  (MPa) represented by  $p = P(0.02P + m)$  and a temperature  $t$  represented by  $0.1875T - 10 < t < 0.5T - 10$  where  $20^{\circ}\text{C} \leq T \leq 60^{\circ}\text{C}$  and represented by  $0.1875T - 10 < t \leq 20^{\circ}\text{C}$  where  $T > 60^{\circ}\text{C}$ .

According to a third aspect of the present invention, there is provided a method of storing a material into which a gas saturates, wherein 0.1 to 1.5 wt% of supercritical carbon dioxide are allowed to

saturate into a pelletized solid resin material, and the solid resin material is stored at a temperature lower than a gas temperature when the carbon dioxide saturates, and at a high gas density.

5           According to a fourth aspect of the present invention, there is provided a method of storing a material into which a gas saturates, wherein 0.1 to 1.5 wt% of supercritical carbon dioxide at a gas density of 0.08 to 0.2 g/cm<sup>2</sup> are allowed to saturate into a  
10 pelletized solid resin material, and the solid resin material is stored at a gas density of 0.7 to 1.0 g/cm<sup>2</sup>.

Other features and advantages of the present invention will be apparent from the following description taken in conjunction with the accompanying  
15 drawings, in which like reference characters designate the same or similar parts throughout the figures thereof.

#### BRIEF DESCRIPTION OF THE DRAWINGS

20           The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

25           Fig. 1 is a view showing an apparatus of an embodiment of the present invention;

Fig. 2 is a view showing the internal structure

of a vessel 1 shown in Fig. 1;

Fig. 3 is a graph showing changes in weights of HIPS materials at atmospheric pressure and room temperature after an inert gas is allowed to saturate  
5 into the materials by the conventional method;

Fig. 4 is a view showing an example in which the apparatus of this embodiment is used as a hopper of an injection foaming machine;

Fig. 5 is a view showing the foamed state of the  
10 section of a foamed product obtained by injection foaming after stored for 1 hr by a storage method of this embodiment;

Fig. 6 is a view showing the foamed state of the section of a foamed product obtained by injection  
15 foaming after left to stand for 1 hr without using the present invention;

Fig. 7 is a view showing the first example of the embodiment; and

Fig. 8 is a view showing the second example of  
20 the embodiment.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

A preferred embodiment of the present invention will now be described in detail in accordance with the  
25 accompanying drawings.

Fig. 1 is a view showing an apparatus of an embodiment of the present invention.



In Fig. 1, reference numeral 1 denotes a vessel; 2, an agitator; 3, a high pressure gas generator; 4, a cooling medium controller; 5, a heater; and 6, a heater controller.

5        Fig. 2 is a view showing the internal structure of the vessel 1 shown in Fig. 1.

In Fig. 2, reference numeral 7 denotes a pipe in which a cooling medium circulates; and 8, agitating blades. In the vessel 1, a solid material into which  
10 an inert gas as a foaming agent saturates is agitated by the agitating blades 8 connected to the agitator 2, and cooled by the cooling medium which is controlled at a predetermined temperature by the cooling medium controller 4 and circulates in the pipe 7. Also, an  
15 inert gas pressurized to a predetermined pressure by the high pressure gas generator 3 is filled into the vessel 1. The heater 5 is installed outside the vessel 1, and the heater controller 6 controls the temperature of the vessel 1.

20        Fig. 7 is a view showing the first example according to the embodiment.

The first example will be explained below with reference to Fig. 7.

As resin materials, three types (A, B, and C) of  
25 high-impact polystyrene (HIPS) were used. Carbon dioxide was used as an inert gas as a foaming agent. Fig. 7 shows the saturation pressure, saturation

temperature, and saturation time by which the carbon dioxide was allowed to saturate into the resin material, and also shows the storage pressure and storage temperature of this example.

5           The storage time in Fig. 7 means the time elapsed since the pressure and time were controlled to the storage pressure and storage time of this example after gas saturation. The weight change is a change ratio calculated by comparing the weight when five minutes  
10 elapsed in atmosphere after gas saturation was complete with the weight measured in atmosphere after the material was stored at the storage pressure and storage temperature of this example, i.e., after the storage time elapsed.

15           The storage time and weight change in Fig. 7 indicate that a change in amount of gas which saturated into the resin material was 1% or less even after the storage time elapsed, i.e., there was almost no change in gas amount.

20           That is, when a resin material into which a gas saturates is stored under the storage conditions of this example, escape of the gas from the resin material can be decreased to a very small amount.

          Practical storage conditions are as follows. A  
25 gas is allowed to saturate into a resin material at a saturation pressure  $P$  (MPa) of 4 (MPa) or more and a temperature  $T$  ( $^{\circ}\text{C}$ ). After that, letting  $m$  ( $-0.05 < m <$

0.2) be a coefficient determined by the material type and the gas saturation time, the resin material is stored in an ambient defined by a pressure  $p$  (MPa) represented by

5 
$$p = P(0.02P + m)$$

and a temperature  $t$  represented by

$$0.1875T - 10 < t < 0.5T - 10$$

where  $20^{\circ}\text{C} \leq T \leq 60^{\circ}\text{C}$

and represented by

10 
$$0.1875T - 10 < t \leq 20^{\circ}\text{C}$$

where  $T > 60^{\circ}\text{C}$ .

Also, the gas saturation amount after storage is 0.1 to 0.4 wt%.

More specifically, 0.1 to 1.5 wt% of  
15 supercritical carbon dioxide are allowed to saturate into a pelletized solid resin material, and the solid resin material is stored at a temperature lower than the gas temperature when the carbon dioxide saturates and at a high gas density.

20 Alternatively, 0.1 to 1.5 wt% of supercritical carbon dioxide at a gas density of 0.08 to 0.2 g/cm<sup>2</sup> are allowed to saturate into a pelletized solid resin material, and the solid resin material is stored at a gas density of 0.7 to 1.0 g/cm<sup>2</sup>.

25 Fig. 5 shows the foamed state of the section of a foamed product obtained by injection foaming after stored for 1 hr by the control method of this example.

Fig. 6 shows the foamed state of the section of a foamed product obtained by injection foaming after left to stand for 1 hr without using the present invention. It is readily understood from comparison of Figs. 5 and 6 that the control method of this example is very effective in maintaining the foamed state.

Fig. 8 is a view showing the second example according to the embodiment.

The second example will be explained with reference to Fig. 8.

Resin materials were six types of materials, i.e., high-impact polystyrene (HIPS), an alloy material (PC/ABS) of polycarbonate and acrylonitrile-butadiene-styrene, polyphenylene ether (PPE), a resin (PPE + GF) formed by filling polyphenylene ether with a glass filler, a resin (PPE + PS) formed by mixing a glass filler in an alloy of polyphenylene ether and polystyrene, and polycarbonate (PC). Carbon dioxide was used as an inert gas as a foaming gas. Fig. 8 shows the saturation pressure, saturation temperature, and saturation time by which the carbon dioxide was allowed to saturate into the resin material, and also shows the storage pressure and storage temperature of this example.

The storage time and weight change shown in Fig. 8 reveal that when the storage pressure and storage temperature were adjusted within the range of

this example by the resin material and saturation time, a change in amount of gas which saturated into the resin material was decreased to 1% or less even when the storage time elapsed.

5           Fig. 3 shows changes in weights of HIPS materials at atmospheric pressure and room temperature after an inert gas was allowed to saturate into the materials by the conventional method. For the sake of convenience of measurement, a point five minutes after gas  
10 saturation is set to 0. As shown in Fig. 3, at any saturation pressure and any temperature, the gas escaped from the material with time.

          Fig. 4 shows an example in which the apparatus of this embodiment is used as a hopper of an injection  
15 foaming machine.

          In Fig. 4, reference numeral 9 denotes an injection foaming machine; 10, a metal foam; 11, a plasticator; 12, a hopper of this embodiment; 13, a gas cylinder; 14, a gas pressurizing apparatus; 15, a gas  
20 saturation vessel; 16 and 17, pumps; 18, a material silo; and 19, a pipe. The hopper 12 has the structures shown in Figs. 1 and 2.

          The foaming process will be described with reference to Fig. 4.

25           A pelletized resin material is stored in the material silo 18. When foaming is to be performed, a necessary amount of the resin material is supplied to

the gas saturation vessel 15 by the pump 17. A gas as  
a foaming material is supplied from the gas cylinder 13  
to the gas saturation vessel 15 after pressurized by  
the gas pressurizing apparatus 14. The gas saturates  
5 into the resin material in the gas saturation vessel 15.  
This resin material into which the gas saturates is  
supplied to the hopper 12 by the pump 16. In the  
hopper 12, the resin material into which the gas  
saturates is stored at the pressure and temperature of  
10 this embodiment. In addition, the resin material is  
supplied to a material feeder of the plasticator 11,  
plasticized and kneaded, and charged into a cavity  
having a desired shape in the metal foam 10. The resin  
into which the gas as a foaming material saturates  
15 starts foaming at the same time the resin is charged  
into the foam. After cooling, the foam is opened to  
extract the foamed product.

As described above, an inert gas such as carbon  
dioxide or nitrogen was allowed to saturate into a  
20 solid polymer material, and the material was stored at  
the pressure and temperature of this embodiment. This  
made it possible to always maintain a predetermined gas  
saturated state. Accordingly, when this embodiment was  
used as a hopper of an injection foaming machine or  
25 extruder, it was possible to always supply a material  
having a stable gas saturation amount. Resin foaming  
and foamed products using this embodiment are harmless

to the environment and superior in dimensional stability and productivity.

In the above embodiment, foam foaming of resin materials is explained. However, the present invention  
5 is of course applicable not only to resin materials but also to rubber materials and so-called polymer materials.

In the examples shown in Figs. 7 and 8, the storage pressure was set at 1 to 2.5 MPa. In practice,  
10 however, the effect of the present invention can be obtained when the storage pressure is set at 0.5 to 4 MPa.

Also, the storage temperature was set at  $-3^{\circ}\text{C}$  to  $15^{\circ}\text{C}$  in the examples shown in Figs. 7 and 8. In  
15 practice, however, the effect of the present invention can be obtained when the storage temperature is set at  $-5^{\circ}\text{C}$  to  $20^{\circ}\text{C}$ .

As has been explained above, high-accuracy foamed products can be obtained with high productivity by the  
20 above embodiment.

As many apparently widely different embodiments of the present invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the  
25 specific embodiments thereof except as defined in the appended claims.